Synopsis of proposed Ph.D. research work

Title of the proposed thesis:

Luminescence Sensing of Hazardous Chemicals by Inorganic-Organic Hybrid Materials: A Mechanistic Study

by

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1. Origin of the research problem

In this decade, one of the worlds' leading challenges is sustainable development. Environmental pollution has become a major issue. Modern developed and developing countries polluting substances like explosives, pesticides, toxic cations, anions, small molecule are serious problem for civilian, commercial, and defense sectors. With the increasing use of polluting materials all over the world, the major concern will be reliably and efficiently detect traces of polluting materials.

Nitro-aromatics(NACs), which are composed of a benzene ring functionalized with several nitro groups, such as 2,4,6-trinitrotoluene (TNT), 2,4,6-trinitrophenol (TNP), 2,4-dinitrotoluene (2,4-DNT), 2,4-dinitrophenol (2,4-DNP), 1,3-dinitrobenzene (1,3-DNB) etc. have become serious pollution sources of groundwater, soils, and other security applications due to their explosive and toxic nature.[1-3]

Pesticides are widely used as herbicides in agriculture to protect crops.[4, 5] Their widespread use in agricultural, pesticides contributes significantly to the contamination of the environment, particularly of soil, surface and underground waters.[6] Organophosphorus compounds and carbamates with high toxicity are the most used pesticides, whose overuse has generated a serious environmental concern and public health risk.[7] Animals and humans are affected by pesticides through food chain. These contaminants pose serious to fatal health hazards, such as asthma, birth defects and deaths. For now, the maximum concentration allowed for common pesticides was set to $3\mu gL^{-1}$ by EPA.[8] So, pesticide control thus has been widely recognized as important for public health.[9]

Metal ions are found naturally in earth. They become toxic when concentrated in human body. Heavy metals enter plant, animal and human tissues via air inhalation, or food chain. Mercury, lead, cadmium, arsenic are well known toxic metal ions for the animal being. Their very low concentration causes various serious diseases for the human body. Cadmium can cause lung cancer, bones and kidney failure.[10] Mercury poisoning hits kidney, brain and central nervous system.[11] Excessive accumulation of lead can cause anaemia, brain dysfunction.[12] Arsenic can cause diarrhea, diabetes and skin cancer.[13, 14] Excess accumulation of Al^{3+} in brain can give birth to the Alzheimer's disease.[15]

Generally speaking anions are very much less toxic than cations.[16] Cyanide anion is an inhibitor of the enzyme cytochrome c oxidase.[17] Fluoride induced nephrotoxicity, dental carriage, fluorosis.[18]

Currently, research focused on rapid detection of hazardous chemicals, such as explosives, pesticides, toxic metal ions and volatile small organic molecules, because of their widespread used

related to human health and environment.[19, 20] In this regard, our major aim is to detect various harmful and toxic substances. Thereby, various types of analytical tools, such as chromatography, gas chromatography coupled with mass spectrometry (GC-MS) and other instrumental analyses, have been utilized for the detection of various substances.[21, 22] Though these techniques are highly selective but some are of high cost and time-consuming; simultaneously, others are not easy to operate.[23] Recently, Luminescence sensing is very superior technique used in research areas because it has many advantages such as high sensitivity, selectivity, easy sample preparation, quick response and could be used in both solution and solid state. Till date different kinds of fluorescent sensing materials have been developed such as polymers, nanomaterials, supramolecular polymers, metal complexes, quantum dots, and glass or gold surfaces for the detection of toxic substances.[24-26] Very recently, increasing investigations have focused on the design of hybrid materials based fluorescence sensors. Hybrid materials are built up of inorganic building units interconnected by organic ligands. They have attracted tremendous research interest due to their potential applications in a wide range of areas such as gas storage/separation, catalysis, sensing, polymerization, and drug delivery. Last couple of years, research on lanthanide ions (Ln^{3+}) based inorganic–organic hybrid materials is an active field in material science due to their important role in lighting technologies, integrated optics and optical telecommunications, solar cells, and biomedicine. Non-lanthanide based hybrid material shows fluorescence behaviour due to $\pi^* \rightarrow$ n and $\pi^* \rightarrow \pi$ transitions of organic lignds. Lanthanide based hybrid material shows unique fluorescence behavior due to “antenna effect” of organic ligands.[27, 28] In antenna effect, the organic ligand is excited to singlet state, from which a part of energy is transferred to the triplet state of lanthanide metal centre through inter-system crossing; as a result metal centre shows its characteristic emission. Based on emission spectrum shift, emitting color change and enhancement or quenching of fluorescence intensity i.e. “turn-on” and “turn-off” responses, different mechanisms of responsive signals have been proposed.

2. Objectives of the work

I propose to study the fluorescence sensing mechanism of different inorganic-organic hybrid materials using different aspects of fluorescence spectroscopy. For this purpose I would like to design various hybrid materials as efficient sensing of target analytes. Our major aims are-

(a) Detailed understanding of fluorescence sensing mechanisms e.g. electron transfer, energy transfer, and fluorescence resonance energy transfers (FRET), etc. and apply it to the study of various inorganic-organic hybrid materials.

(b) Design and synthesis of new inorganic-organic hybrid materials for specific purposes using different organic ligands for better sensitivity of various harmful and toxic substances.

(c) Determination of the structure of the material by powder XRD, single crystal XRD etc.

(d) Characterization of the hybrid materials by using TGA, IR, UV-Visible absorption and fluorescence spectroscopy.

(e) Theoretical calculation for the understanding of optical properties of the materials.

3. Methodology

(i) Solvothermal or hydrothermal tecnnique

Solvothermal technique is very useful for synthesizing hybrid materials above room temperature and at pressure greater than 1 atm in a closed system. The solvothermal or hydrothermal reaction can be considered as any heterogenous chemical reaction in presence of nonaqueous or aqueous solvent. The success of hydrothermal synthesis depends on the selection of ligands that are both reactive and cost effective as well as appropriate conditions which are temperature, pH and reagent concentration.

(ii) UV-visible absorption spectroscopy

First, samples are prepared for measurement; liquids are placed in a cuvette, and solids samples are placed in a solid sample holder. The sample container must allow passing of UV radiation from 200-700nm. A complete spectrum of the absorption is recorded at all wavelengths. Ultraviolet-visible spectrophotometer can be used to determine molar excitation coefficient/or concentration of the sample.

(iii) Fluorescence spectroscopy

Fluorescence spectroscopy is an analytical technique for identifying and characterizing minute amounts of a substance by excitation of the substance with a beam of ultraviolet light. In fluorescence measurement, the excitation wavelength is fixed and the emission wavelength varies, while in fluorescence excitation measurement the emission wavelength is fixed and the excitation wavelength is varies across a region of interest. Fluorescence intensity is plotted with respect to the wavelength obtained from collecting monochromator. Different aspects of Fluorescence

spectroscopy such as intensity, lifetime, and anisotropy etc. of fluorescent probe molecule will change with the interaction of analytes. By monitoring the change of different aspect we can recognize various analytes.

(iv) Lifetime measurements

The radiative emissions of light from a molecule after excitation are based on multiparameter (i.e. excitation, emission, polarization etc.). A steady state measurement of the fluorescence emission (intensity vs wavelength) gives an average and also relative representation. The fluorescence lifetime gives an absolute (independent of concentration) measure and allows a dynamic picture of the fluorescence to be obtained. The emission of a fluorophore is highly influenced by its environment or the presence of other interacting molecules which can affect the non radiative radiation. So, lifetime measurements are useful in molecular interactions.

4. Future Prospect

With the understanding of sensing mechanism and the molecular level interaction of the sensors and analytes, we shall design (or propose) sensor materials for specific purposes. Further, we shall plan to construct sensor devices for different purposes. We believe, our material or device will be not only effective but also be low cost and time saving. For example, our low cost materials which could be an excellent sensor of nitro-explosives and a device made of that material might replace the canines, presently utilised for explosive detection with huge expense of money. A good sensor proposed by us for biomolecules could be utilized for clinical tests which are presently very expensive. A sensor for pesticides could be used to control the quality of foods available in our market. A sensor for pollutant may be designed for the monitoring of different environmental parameters. A toxic metal ion sensor may be designed for the monitoring of quality of drinking water.

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